NASA-CR-194710

NASA CONTRACTOR REPORT

THEORETICAL RESEARCH PROGRAM TO STUDY CHEMICAL REACTIONS IN AOTV BOW SHOCK TUBES

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Prepared for

Ames Research Center
under Cooperative Agreement NCC2-371

National Aeronautics and
Space Administration

Ames Research Center
Moffett Field, California 94035

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CONTRACT NAS2–

NASA

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Theoretical Research Program to Study Chemical Reactions in AOTV Bow Shock Tubes		5. Report Date 10 December 1993 6. Performing Organization Code
7. Author(s) Peter R. Taylor		8. Performing Organization Report No. 10. Work Unit No.
9. Performing Organization Name and Address Eloret Institute 3788 Fabian Way Palo Alto CA 94303		11. Contract or Grant No. NCC2-371 13. Type of Report and Period Covered 11/1/85 to 08/31/93
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20456		14. Sponsoring Agency Code

15. Supplementary Notes

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16. Abstract

The main focus of this work was the development, implementation, and calibration of methods for performing molecular electronic structure calculations to high accuracy. These various methods were then applied to a number of chemical reactions and species of interest to NASA, notably in the area of combustion chemistry.

Among the development work undertaken was a collaborative effort to develop a program to efficiently predict molecular structures and vibrational frequencies using energy derivatives. Another major development effort involved the design of new atomic basis sets for use in chemical studies: these sets were considerably more accurate than those previously in use. Much effort was also devoted to calibrating methods for computing accurate molecular wave functions, including the first reliable calibrations for realistic molecules using full CI results.

A wide variety of application calculations were undertaken. One area of interest was the spectroscopy and thermochemistry of small molecules, including establishing small molecule binding energies to an accuracy rivaling, or even on occasion surpassing, the experiment. Such binding energies are essential input to modeling chemical reaction processes, such as combustion. Studies of large molecules and processes important in both hydrogen and hydrocarbon combustion chemistry were also carried out. Finally, some effort was devoted to the structure and spectroscopy of small metal clusters, with applications to materials science problems.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Molecular electronic structure calculations combustion chemistry molecular structures vibrational frequencies	unclassified, unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
unclassified	unclassified		

*For sale by the National Technical Information Service, Springfield, Virginia 22161

THEORETICAL RESEARCH PROGRAM TO STUDY CHEMICAL REACTIONS IN AOTV BOW SHOCK TUBES

Final Technical Research Report
Cooperative Agreement No. NCC2-371

for the period

November 1, 1985 - August 31, 1993

Submitted to

National Aeronautics and Space Administration
Ames Research Center
Moffett Field, California 94035

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10 December, 1993

The main focus of the work carried out under Cooperative Agreement NCC2-371 was the development, implementation, and calibration of methods for performing molecular electronic structure calculations to a high degree of accuracy. These various methods were then applied to a number of chemical reactions and species of interest to NASA, notably in the area of combustion chemistry.

Among the development work undertaken was a collaborative effort (with several Scandinavian quantum chemists) to develop a program to efficiently predict molecular structures and vibrational frequencies using energy derivatives. This program exploits molecular symmetry using symmetry-adapted functions and can handle MCSCF wave functions. These combination of capabilities is unique. Another major development effort involved the design of new atomic basis sets for use in chemical studies. These "atomic natural orbital" sets were considerably more accurate than those previously in use, and they were utilized extensively by the entire NASA-Ames Computational Chemistry Branch in performing accurate quantum chemical calculations, as well as by outside researchers. Much effort was also devoted to calibrating methods for computing accurate molecular wave functions, including the first reliable calibrations for realistic molecules using full CI results. The full CI calculations were possible only on the NAS Facility CRAY-2 at the time (1985-1986), and they attracted considerable attention.

A wide variety of application calculations were undertaken. One area of interest was the spectroscopy and thermochemistry of small molecules, including establishing small molecule binding energies to an accuracy rivaling, or even on occasion surpassing, the experiment. Among the species studied was the radical CN, whose binding energy had been a long-standing controversy in the spectroscopy community, and the CH bond energy in acetylene, where two sets of conflicting experimental results were available. Our calculations resolved both these controversies. It may be noted that such binding energies are essential input to modeling chemical reaction processes, such as combustion. Among the more important

spectroscopic investigations were the rotation-vibration intensities (dipole moment function) of OH, a species important as a thermometric probe, and the electronic spectroscopy of diatomic aluminum halides, with relevance to radiation signatures. Studies of large molecules and processes important in both hydrogen and hydrocarbon combustion chemistry were also carried out, including binding energy studies of CH and NH bonds, and mechanistic studies of reactions important in prompt NO_x formation ($CH + N_2$) and in hydrocarbon combustion (acetylene pyrolysis). Finally, some effort was devoted to the structure and spectroscopy of small metal clusters, with applications to materials science problems, and to computing properties that influence nonlinear optical properties: polarizabilities and hyperpolarizabilities.

The following publications have resulted from this work:

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